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1964

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Abstract

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PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE INFLUENCE OF THE STRUCTURE OF POROUS BODIES ON THE VALUE OF THE SPECIFIC SURFACE AREA DETERMINED BY THE GAS-PERMEABILITY METHOD

(Presented by Academician I. K. Kikoin, November 5, 1963)

As is known, when determining the specific surface area by the gas-permeability method, use is made of the dependence of the magnitude of the gas flow through a porous medium on its specific surface area. This dependence may be represented in the form (see, for example, $^{(1,2)}$)*:

$$Q = Q_c + Q_\mathrm{v} = A\frac{\delta^2 \Delta p}{\sqrt{\pi\mu RT}\,(1-\delta)\,S_0 l} + B\frac{\delta^3}{(1-\delta)^2 S_0^2}\,\frac{\bar{p}\Delta p}{\eta RT}\,\frac{\mathrm{mol}}{\mathrm{sec}\cdot\mathrm{cm}^2}, \qquad (1)$$

where S_0 is the specific surface area of the sample in $\mathrm{cm}^2/\mathrm{cm}^3$; l is the length of the sample; δ is the porosity; Δp is the pressure drop across the sample; $\bar{p}$ is the mean pressure in the sample; η is the viscosity coefficient.

The quantities A and B entering equation (1) are usually expressed through parameters characterizing the structure of the porous medium $^{(1)}$:

$$A = \frac{8\sqrt{2}}{3}\,\frac{\delta_1}{k_1 b}; \qquad B = \frac{1}{k} = \frac{1}{k_0 b}, \qquad (2)$$

where k is the so-called Kozeny constant $\left(k = 5.0 \pm 10\%\,^{(2)}\right)$; k_1 is the shape factor for molecular flow; k_0 is the shape factor for viscous flow; δ_1 is a parameter taking into account the character of the interaction of molecules with the wall. According to Carman' s definitions, the complex of constants $\delta_1/k_1 b$ for slip flow in the case of normal structures is equal to 0.45.

b is the tortuosity factor, taking into account the real path length of gas molecules in the porous medium. On the basis of extensive experimental material, Carman $^{(1)}$ showed that for so-called normal structures b has a value close to 2. However, the values of the tortuosity factor measured for real

Fig. 1

Figure 1: Fig. 1

porous media by diffusion or electrical-conductivity methods vary within very wide limits and in some cases exceed the value $b = 2$ by a factor of 2-100 (3). Obviously, in these cases the concept of tortuosity as defined above loses its physical meaning, since it is difficult to imagine a porous system whose true channel length is tens of times greater than its geometrical size. Therefore the quantity b should rather be regarded as a certain structural parameter characterizing the features of the structure of the given porous medium (tortuosity in the usual sense, the influence of local constrictions connecting individual pores-chambers, the presence of dead ends and closed cavities, etc.).

It should be noted that in some works (4,5), where the flow of rarefied gases through a porous body is considered, the quantity A is determined purely theoretically in such a way that the specific structure of real porous bodies is not taken into account at all, i.e., the expression for the flow does not include—gives a structural parameter related to the shape, number, or length of the pore channels.

As was already noted in work (6), incorrect allowance for the structural features of real porous media leads to the appearance of a strong dependence of the value of the specific surface S_D, determined with the aid of the Deryagin formula (the molecular term of expression (1) at $A = 24\sqrt{2}/13$), on the porosity of the specimen; moreover, the values of S_D often have no physical meaning whatever, since they exceed severalfold the total surface of the powder,

Fig. 1. Effect of the porosity of a compact on the values of the specific surface calculated according to Deryagin (S_D) and according to Khodakov (S_L and $S_{L=2\mu}$).
a—effect of the porosity of the specimen on the value L, calculated according to Khodakov; *b*—porous calcium fluoride, $S_{\text{BET}} = 3.1 \cdot 10^5$ cm^{-1}; $\gamma = 3.15$ g/cm^3; *c*—Fe I, $S_{\text{BET}} = 13.7 \cdot 10^5$ cm^{-1}; $\gamma = 7.8$ g/cm^3; *d*—Fe II (oxidized), $S_{\text{BET}} = 13.9$ cm^{-1}; $\gamma = 4.2$ g/cm^3.

determined by the BET method. The existence of such, and even stronger, dependence (S_D reaches $10 S_{\text{BET}}$) is confirmed by our measurements on a number of nonmetallic and especially metallic powders. Some of these results are

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* With this form of notation it is assumed that the total flow in the porous medium can be represented as the sum of the molecular (Q_m), or so-called slip flow (Q_c) (the latter, according to (1), amounts to $\approx 0.9 Q_m$), and viscous (Q_{v}) flows over the entire pressure range. A special experimental check has shown that for most porous media (at $\delta < 0.7$-0.8) this assumption is valid within the accuracy required for determining the specific surface area ($\pm 5.0\%$).

presented in Fig. 1.

It is strange that the authors of works (4) did not pay attention to the existence of such a strong dependence of S_D on δ, which practically devalues the method of determining specific surface proposed by them*. Numerous attempts (see, for example, (8)) to take into account the dependence of S_0 on δ by means of various kinds interpolation expressions, as experience shows, are either untenable or suitable only for a given type of powder.

In [6] an attempt is made to estimate the influence of narrow channels connecting chamber pores (an analogous consideration was made earlier [9]) on the value of the specific surface determined by means of Deryagin' s formula. For this purpose a certain characteristic dimension L, associated with the particular structure of the real porous medium, is introduced. Then the final expression for calculating the specific surface (for $S_0 \geqslant 1.3/\gamma$ (m^2/g), where γ is the density of the substance) takes the form

$$S_L = 2\sqrt{2}\sqrt{\delta S_D/L(1-\delta)} = \sqrt{\delta S_D/(1-\delta)}\,2\sqrt{2}/L. \tag{3}$$

The quantity L is determined experimentally by comparing the permeability k_1/k_2 at two substantially different mean gas pressures (k_1 at $p_1 = 760$ mm Hg and k_2 at $p_2 \simeq 10$ mm).

An expression analogous to (3) can easily be obtained in an elementary way from equation (1). We introduce the notation:

$$S_{\mathrm{v}} = \sqrt{\frac{\delta^3 p \Delta p B}{(1-\delta)^2 l R T Q_{\mathrm{v}}}}, \qquad S_{\mathrm{m}} = \frac{A\delta^2 \Delta p}{\sqrt{\pi \mu R T}\, l(1-\delta) Q_{\mathrm{c}}}, \tag{4}$$

where S_{v} and S_{m} are the values of the specific surface S_0, determined respectively from the viscous and molecular (slip-flow) terms of the complete flow equation (1). Expression (1) may be written in the form

$$Q = Q_{\mathrm{v}} + Q_{\mathrm{c}} = Q_{\mathrm{c}}(1 + Q_{\mathrm{v}}/Q_{\mathrm{c}}) = Q_{\mathrm{c}}(1 + \bar{\alpha} p), \tag{5}$$

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* It should be noted that, when comparing surface values according to Carman and according to Deryagin in works (4), by the Carman method for some reason one always means the calculation of S_0 from the expression for viscous flow, which, for obvious reasons, is inapplicable for fine powders (with $S \geq 1$ m^2/g). At the same time, the calculation method proposed as early as 1947–1948 by Rizhden, Carman, and Archell, which takes into account the contribution of slip flow (molecular flow), is completely ignored (7). In the general case, as is known, it is proposed to carry out the calculation from the complete flow equation (1).

where $\alpha = \frac{1}{p}\frac{Q_\mathrm{v}}{Q_\mathrm{c}}$. Hence $Q_\mathrm{v} = \bar{\alpha} p Q_\mathrm{c}$. Now S_v can be written in the following way:

$$S_\mathrm{v} = \sqrt{\frac{\delta^3 \Delta p B}{(1-\delta)^2 \alpha l R T Q_\mathrm{c}}} = \sqrt{\frac{\delta S_\mathrm{m}}{1-\delta}}\sqrt{\frac{B}{A\alpha\eta}}\sqrt{\frac{\pi\mu}{RT}}. \tag{6}$$

The quantity α, like L, is determined experimentally from the ratio of permeabilities at different mean gas pressures in the porous medium.

Table 1

Sample	δ	b	$S_0 \cdot 10^{-5}$ cm^{-1}, by (1)	$S_0 \cdot 10^{-5}$ cm^{-1}, by (1), corrected for b_1	$S_\mathrm{BET} \cdot 10^{-5}$ cm^{-1}
Reactive nickel	0.42	1.9	0.32	0.34	0.40
Reactive nickel	0.27	3.5	0.68	0.37	0.40
Iron	0.69	1.9	9.6	10.1	13.0
Iron	0.45	3.2	17.2	10.7	13.0
Iron II (oxidized)	0.61	6.0	35.0	11.6	14.0
Iron II (oxidized)	0.45	11.0	73.0	13.3	14.0

Substituting into (6) the values of the constants (2) and taking into account that $S_D = 1.54\,S_\mathrm{m}$ [1], one can obtain an expression relating the quantities L and α: $L = 5.4 \cdot 10^5 \alpha\eta\sqrt{T/\mu}$, or, for measurements in air at room temperature, $\alpha = 0.313 \cdot 10^3 \alpha$. It should be emphasized that, since every body pressed from powder represents a unique porous structure, the quantities L or α can characterize only the properties of the given packing and must be determined for each sample tested. (Figure 1a shows the dependence of the quantity L on the porosity of the compact for various powders.) The assertion contained in [6] that the permeability ratio k_1/k_2 for any porous media with $S_0 \geqslant 1.3/\gamma$ (m^2/g) may be regarded as constant (this is equivalent to the assertion that $Q_\mathrm{v}/\bar{p}Q_\mathrm{c} \simeq$ const!) and equal to 1.5 (i.e., with $L \simeq 2\mu$) is fundamentally incorrect, and in practice leads to a loss of sensitivity of expression (3) to changes in the mean pore radius. Indeed, the results given in [6] and in Fig. 1 for the calculation of $S_{L=2\mu}$ by expression (3) (with $L = 2\mu$) are almost independent of the porosity of the sample; however, this occurs only because the method has become insensitive to changes in the mean pore radius when δ changes. It is evident from Fig. 1 that such "coarsening" of the method is inadmissible, since it leads to su-

substantial and random distortions of the absolute value of the measured surface (from 0.15 to 0.6 S_{BET}).

From comparison of expressions (3) and (6) it follows that determination of S_L by formula (3) is, in essence, equivalent to calculating S_0 from the viscous part of the flow equation (1). However, as is seen from Fig. 1, such a method of calculation only somewhat weakens the dependence on the porosity of the specimen, but does not make it possible to eliminate it.

The reason for the experimentally observed strong dependence of S_0 on δ is the change in the structural parameter with change in the porosity of the compact. Indeed, the quantity b enters into the calculation of S_0 both according to equation (1) and on the basis of expression (6), and also in fact affects the determination of S_0 according to the "corrected" expression (3).

The assumptions made above concerning the change in the magnitude of the structural parameter with change in δ were confirmed by direct determinations of b by measuring the coefficient of self-diffusion of CO_2 in a porous medium. In addition, values of b were extracted from the measured values of Q_{v} and Q_{s} by simultaneous solution of equations (4) (an analogous procedure was used in works [10]) with fixed shape constants, and also from data on mercury intrusion into porous specimens. The values of b obtained by different methods agree well. Part of the results obtained is presented in Table 1.

It is evident from the table that: 1) the value of b changes substantially when the porosity of the specimen changes; 2) the values of the surface S_0, calculated from expression (1) (taking into account the true value of the parameter b), are practically stable, do not depend on porosity, and agree satisfactorily with the values S_{BET} obtained by the adsorption method.

The authors express their deep gratitude to Acad. I. K. Kikoin and Yu. M. Kagan for their attention to this work.

Received
30 IV 1963

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